PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
SC12991CF/PCT		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/EP2005/001511	15/02/2005	17/02/2004
Applicant		
FREESCALE SEMICONDUCTOR, INC.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
      [ ] The international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
   b. [ ] With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. [ ] **Certain claims were found unsearchable** (See Box II).

3. [ ] **Unity of invention is lacking** (see Box III).

4. With regard to the **title,**
   [ ] the text is approved as submitted by the applicant.
   [X] the text has been established by this Authority to read as follows:

   IMMERSION LITHOGRAPHY TECHNIQUE AND PRODUCT USING A PROTECTION LAYER COVERING THE RESIST

5. With regard to the **abstract,**
   [X] the text is approved as submitted by the applicant.
   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regard to the **drawings,**
   a. the figure of the **drawings** to be published with the abstract is Figure No. 2
      [ ] as suggested by the applicant.
      [X] as selected by this Authority, because the applicant failed to suggest a figure.
      [ ] as selected by this Authority, because this figure better characterizes the invention.
   b. [ ] none of the figures is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/001511

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G03F7/09 G03F7/11 G03F7/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, INSPEC, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2001/044077 A1 (TAN ZOILO CHEN HO) 22 November 2001 (2001-11-22) paragraphs '0008!, '0014! - '0020!; figure 2	6-8,10
X	US 5 326 675 A (NIKI HIROKAZU ET AL) 5 July 1994 (1994-07-05) column 3, lines 6-34 column 7, lines 34-42 column 19, lines 5-65	6
X	US 2002/076626 A1 (MONTGOMERY CECILIA ANNETTE ET AL) 20 June 2002 (2002-06-20) paragraphs '0009! - '0011!, '0031!	6

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 July 2005	24/08/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Müller-Kirsch, L

1

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/001511

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 0184, no. 23 (P-1783), 8 August 1994 (1994-08-08) & JP 06 130657 A (MITSUBISHI RAYON CO LTD; others: 01), 13 May 1994 (1994-05-13) abstract	6
A	SWITKES M ET AL: "Extending optics to 50 nm and beyond with immersion lithography" J. VAC. SCI. TECHNOL. B, MICROELECTRON. NANOMETER STRUCT. (USA), JOURNAL OF VACUUM SCIENCE & TECHNOLOGY B (MICROELECTRONICS AND NANOMETER STRUCTURES), NOV. 2003, AIP FOR AMERICAN VACUUM SOC, USA, vol. 21, no. 6, September 2003 (2003-09), pages 2794-2799, XP002285381 ISSN: 0734-211X page 2794, column 2, line 27 - page 2795, column 1, line 2 page 2797, column 2, lines 2-15 page 2798, column 2, line 34 - page 2799, column 1, line 3	1,6
A	US 4 346 164 A (LOEBACH ERNST W ET AL) 24 August 1982 (1982-08-24) column 3, line 57 - column 4, line 13	1,6
P,X	US 2004/075895 A1 (LIN BURN JENG) 22 April 2004 (2004-04-22) adressing several problems in immersion lens lithography: PHOTORESIST outgassing problem, fluid circulation, fluid filtering for maintaining fluid particle free, temperature management, circulation of paragraph '0026!	1,6

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP2005/001511

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2001044077 A1	22-11-2001	AU 4246500 A	02-11-2000
		WO 0063747 A1	26-10-2000
		US 2004265706 A1	30-12-2004
		US 2002071995 A1	13-06-2002
		US 2002076626 A1	20-06-2002
US 5326675 A	05-07-1994	JP 3281053 B2	13-05-2002
		JP 5216244 A	27-08-1993
		KR 9506953 B1	26-06-1995
		US RE35821 E	09-06-1998
US 2002076626 A1	20-06-2002	US 2002071995 A1	13-06-2002
		US 2001044077 A1	22-11-2001
		EP 1459131 A1	22-09-2004
		JP 2005510761 T	21-04-2005
		WO 03046658 A1	05-06-2003
		US 2004265706 A1	30-12-2004
		EP 1405142 A1	07-04-2004
		JP 2004534969 T	18-11-2004
		WO 03007081 A1	23-01-2003
		AU 4246500 A	02-11-2000
		WO 0063747 A1	26-10-2000
JP 06130657 A	13-05-1994	NONE	
US 4346164 A	24-08-1982	US 4509852 A	09-04-1985
US 2004075895 A1	22-04-2004	NONE	

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP2005/001511	15.02.2005	17.02.2004

International Patent Classification (IPC) or both national classification and IPC
G03F7/09, G03F7/11, G03F7/20

Applicant
FREESCALE SEMICONDUCTOR, INC.

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA"). However, this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notifed the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of three months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA:

European Patent Office - P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040 Tx: 31 651 epo nl
Fax: +31 70 340 - 3016

Authorized Officer

Müller-Kirsch, L

Telephone No. +31 70 340-4867

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/EP2005/001511

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This opinion has been established on the basis of a translation from the original language into the following language , which is the language of a translation furnished for the purposes of international search (under Rules 12.3 and 23.1(b)).

2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ in written format

   ☐ in computer readable form

   c. time of filing/furnishing:

   ☐ contained in the international application as filed.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

4. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/EP2005/001511

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-5,9
	No:	Claims	6-8,10
Inventive step (IS)	Yes:	Claims	1-5,9
	No:	Claims	6-8,10
Industrial applicability (IA)	Yes:	Claims	1-10
	No:	Claims	

2. Citations and explanations

see separate sheet

1

The following documents D1-D2 are referred to in this communication; the numbering will be adhered to in the rest of the procedure:

D1: US-A-20010044077
D2 Switkes et al. JVSTB 21 (2003), p. 2794

2

The document D2 is regarded as being the closest prior art to the subject-matter of **claim 1**, and shows (the reference in parentheses applying to this document):

An immersion lithography method in which an optical exposure system is used to expose a photoresist layer during an exposure period, an immersion medium is inserted between the optical exposure system and the photoresist layer to be exposed and, after exposure, the photoresist layer is developed using a developer (p. 2794).

D2 describes the preamble of claim 1, an immersion lithography method using a resist which is developed after exposure.

The difference between **D2** and claim 1 is the presence of a a protection layer, the protection layer being transparent to the exposure wavelength and impervious to the immersion liquid.

The subject-matter of claim 1 is therefore new (Article 33(2) PCT).

The problem which is solved by this difference is to make the resist assembly chemically inert to the immersion liquid so that the resist does not dwell and is not dissolved in the liquid **during exposure**.

Document **D1** discloses the features of the difference: a thin aluminium layer is would not be in the liquid and would be impervious to it. However, document D1 mentions only the protection against moisture in storage ambiance. That does not mean, that such a protection layer is suitable for the presence of an immersion liquid under exposure

conditions. Therefore, the problem which is solved by the protection layer mentioned in document D1 is different to the above described problem solved by claim 1 and the application of the protection layer to the immersion lithography process of document D2 is not obvious, although document D2 addresses the problem explicitly (p. 2794, col. 2, l. 27-p. 2795, col. 1, l. 1).

Claims 2-5 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

3

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 6-8 and 10 is not new in the sense of Article 33(2) PCT.

3.1 Document D1 discloses all features of claim 6, namely:
An intermediate product **suitable for** exposure in an immersion lithography process, the product consisting of a substrate (12) bearing a photo resist layer (16), the surface of the photo resist layer remote from the substrate being covered by a shield layer (20) which is transparent at the exposure wavelength used in the immersion lithography process (par 14) and substantially impervious to the immersion medium (par 15, 17).

Preliminary studies have shown that a large variety of 193 nm resists are suitable for immersion light lithography without adaptations (see e.g. document D2, page 2797, lines 2-15).

Consequently, claim 6 is not novel. Alternative objections could be based on D2, see passages in the search report. The applicant should note that water-soluble protective layers may be insoluble in oil used which can be also used as immersion liquid.

3.2 Medium (par 7) D1 discloses that the shield layer can be chemically insoluble (par 20).

3.3 Claims 7 and 10 are equally disclosed to in document D1.

4

An independent claim combining the features of dependent claim 9 would not have been known from the prior art available. Such a claim would have been therefore novel and

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY (SEPARATE SHEET)

International application No.

PCT/EP2005/001511

inventive.

EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

PUBLICATION NUMBER : 06130657
PUBLICATION DATE : 13-05-94

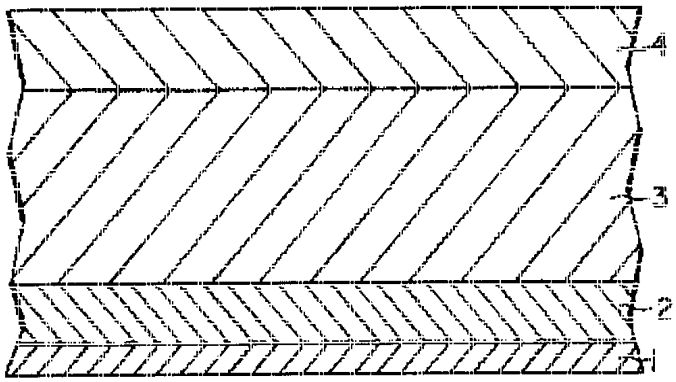
APPLICATION DATE : 20-08-91
APPLICATION NUMBER : 03208325

APPLICANT : NITTO CHEM IND CO LTD;

INVENTOR : KOYANAGI SEIYA;

INT.CL. : G03F 7/004 C09K 3/16 G03F 7/09
H05F 1/02

TITLE : DRY FILM RESIST



ABSTRACT : PURPOSE: To prevent deposition of foreign matter such as dust on a base film due to electrostatic effect by forming an antistatic layer consisting of tetracyanoquinodimethane complex (TCNQ complex) on the surface of the base film.

CONSTITUTION: A resist layer 3 is formed on a base film 2 and further a cover film 4 is formed thereon. On the opposite surface of the base film 2, an antistatic layer 1 consisting of TCNQ complex is formed. This antistatic layer 1 consists of 0.5-80wt.% TCNQ complex and 99.5-20wt.% transparent resin and has 0.05-0.5μm thickness and 10^5-$10^8\Omega/cm^2$ surface resistance. This antistatic layer 1 is formed by dissolving a TCNQ complex and transparent resin in a solvent, applying the soln. on the other surface of the base film, and then drying. The TCNQ complex to form the antistatic layer 1 gives excellent antistatic effect without decrease of the effect even in a low humidity environment.

Extending optics to 50 nm and beyond with immersion lithography

M. Switkes,[a] R. R. Kunz, M. Rothschild, and R. F. Sinta
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02420

M. Yeung and S.-Y. Baek
Department of Manufacturing Engineering, Boston University, Brookline, Massachusetts 02446

(Received 7 July 2003; accepted 15 September 2003; published 5 December 2003)

Numerical imaging simulations demonstrate the capability of immersion lithography to print features smaller than 45 nm (35 nm) with good depth of focus at a vacuum wavelength of 193 nm (157 nm). The optical impact of index variation of the immersion liquid is simulated and found to be a shift of focus of 1 nm for each 1 ppm change in the bulk index of the liquid. For an index which varies through the thickness of the liquid (e.g., due to nonuniform temperature), the focus shift is found to be proportional to the total change in optical path length (OPL), with a 1 nm change in OPL leading to a ~1.5 nm focus shift at 1.3 numerical aperture. A focus offset of 1–3 nm can be expected due to heating during scanning exposure. The possible formation of nanobubbles at resist surfaces is also discussed. While simulations show that even 10 nm thick bubbles at the surface of the resist cause 30% modulation in the aerial image intensity, no evidence of bubbles is seen in open frame immersion exposures. Imaging of 100 nm features is shown using an immersion contact phase-edge technique, with no evidence of bubbles or adverse liquid–resist interactions. Finally, we describe progress in the search for low absorbance liquids for use at 157 nm. Liquid purity, including dissolved O_2 and H_2O, is found to be critical. The current absorbance record, $0.64 \pm 0.07\ cm^{-1}$, held by perfluorotriglyme ($CF_3[OCF_2CF_2]_3OCF_3$), is enough for a 350 μm working distance at 95% transmission. [DOI: 10.1116/1.1624257]

I. INTRODUCTION

Immersion microscopy was invented over 150 years ago when the benefit of filling the space between the microscope's final optical element and its target with a high index liquid was realized. Because the wavelength of light in a fluid is reduced from the vacuum wavelength λ, the resolution W can be improved by a factor of the index of refraction of the fluid n:

$$W = k_1 \frac{\lambda/n}{\sin\theta}, \tag{1}$$

where θ is the angular half aperture of the lens and k_1 is the resolution coefficient. The idea of applying the benefits of immersion to projection lithography is likewise not new. Immersion lithography had emerged in the patent literature[1] by 1984 and in regular open literature[2] by 1987. Several small scale studies of immersion patterning[3–6] were undertaken in the 1980s and early 1990s but did not progress beyond the proof-of-concept stage; other factors on the right-hand side of Eq. (1) presented easier targets for resolution improvement. Now, with both $\sin\theta$ and k_1 approaching 85% of their physical limits, and a lack of transparent optical materials below ~150 nm that provides serious technical challenges to further reduction of λ, immersion has become a serious candidate for extending optical lithography to 50 nm and below.

Beyond improvements in resolution, immersion is attractive because the vacuum wavelength of the radiation remains unchanged, allowing much of the technology developed for dry lithography at that wavelength to be carried over into immersion. Light sources, optical materials and coatings, purging and contamination control systems, and perhaps even resists can be used essentially unchanged. Masks will likewise remain unchanged except for the reduction in feature size allowed by the improved system resolution. The novel elements in immersion lithography are essentially three. First, a new lens design is required to take advantage of the immersion liquid. Several designs for full-field immersion lenses with numerical aperture (NA)$=n\sin\theta$ up to 1.2 have been presented[7,8] by lithographic tool makers. Second, a liquid dispensing and recovery system is required, and several concepts for this have also been proposed[7,9] and are currently under study.

The final and perhaps most critical element of immersion lithography is the immersion liquid itself. As a component of a high-precision optical system as well as of the entire semiconductor process flow, the liquid must fulfill many requirements. Physically, it must be transparent at the exposure wavelength, have a high enough index to make the resolution improvement worthwhile, and have low viscosity to facilitate high speed scanning. Additionally, the liquid should be nontoxic and must be compatible with cleanroom processing. For all of these reasons, water is a very attractive candidate liquid at 193 nm. It has low absorbance,[10] $\alpha = 0.036\ cm^{-1}$ (base 10) and a relatively high index,[11] $n = 1.44$, along with low viscosity and familiarity in the semiconductor manufacturing process. In addition to its physical properties, the immersion liquid must be chemically compatible with the photoresist and with the final lens element. It must not interact with the photoresist in any way which impedes high resolu-

[a]Electronic mail: mswitkes@ll.mit.edu

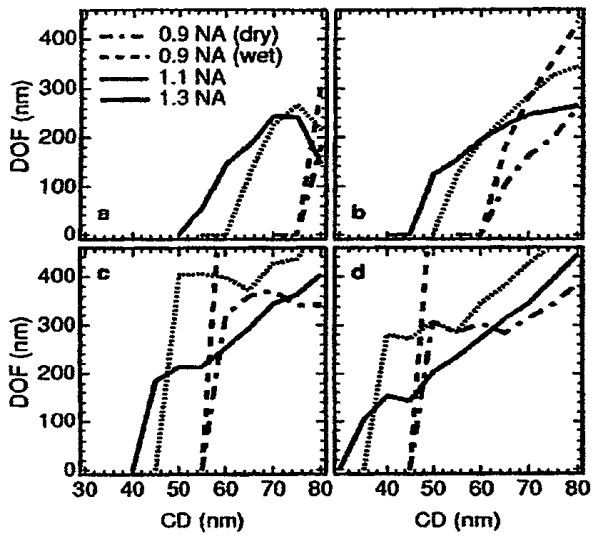


FIG. 1. Numerical simulations of printing dense line and space patterns for NAs of 0.9 (immersion and dry), 1.1, and 1.3. The depth of focus at 10% exposure latitude is shown as a function of the feature size. (a) Binary mask at 193 nm with annular illumination (σ=0.4–0.6). (b) Binary mask at 157 nm with annular illumination. (c) Alternating phase shift mask at 193 nm with conventional illumination (σ=0.3). (d) Alternating phase shift mask at 157 nm.

tion imaging, and must not contaminate the lens over the life of the exposure tool.

In this article, we address further concerns about the homogeneity of the liquid index due to temperature variations as well as the possibility of bubble formation in the liquid. We also report our initial imaging results using water immersion phase-edge contact printing. At 157 nm, research has focused on identifying suitably transparent fluids. Fluorinated fluids have shown some promise as immersion liquids,[12] but absorbance has remained too high to permit practical working distances. Here we report on our progress in identifying and purifying suitable fluorinated liquids for use at 157 nm.

II. IMAGING SIMULATIONS

To assess the potential of immersion lithography, we performed numerical imaging simulations using the model described fully in Ref. 13 to calculate exposure-defocus trees for dense line and space patterns with a ±10% critical dimension (CD) tolerance. This Maxwell vector model accounts for thin-film interference as well as polarization and other high NA effects, and all simulations assume randomly polarized light. Figure 1 shows the depth of focus (DOF) as a function of the nominal linewidth for an exposure latitude of 10%, for conventional dry lithography with NA=$n \sin\theta$ of 0.9 and water immersion lithography with NAs of 0.9–1.3, both using annular illumination at σ=0.4–0.6. At λ=193, 0.9 NA has essentially no DOF below 75 nm with a simple binary mask while water immersion with the same value of $\sin\theta$ (NA=1.3) allows printing with good DOF below 60 nm [Fig. 1(a)]. At λ=157, the improvement is similar with NA=1.3 allowing printing below 50 nm compared to the 65 nm available with ultrahigh NA dry lithography [Fig. 1(b)]. Resolution can be further improved using the whole suite of resolution enhancement techniques developed for dry lithography which carry over directly into immersion. For example, using an alternating phase shift mask (altPSM) with conventional illumination (σ=0.3), immersion allows λ=193 to extend to 45 nm features and λ=157 to 35 nm features as seen in Figs. 1(c) and 1(d). We note that, according to the *International Technology Roadmap for Semiconductors* (Semiconductor Industry Association, San Jose, CA, 2002, http://public.itrs.net/), 45 nm lithography will be needed starting in the year 2010, and 32 nm lithography starting in 2013. Even in the absence of the highest NAs, immersion will allow printing down to ~50 nm at 193 nm using NAs for which full-field lens designs are currently available.[7,8]

III. INDEX VARIATION DUE TO HEATING

One major concern in immersion lithography is distortion of the image due to index inhomogeneities in the liquid. Variation in the index of the immersion fluid causes, to first order, defocus in the image,[14] along with small amounts of spherical and higher order abberations.[13] With a 1 mm working distance and $\sin\theta$=0.9, our simulations show that a change in the bulk liquid index of 1 ppm causes ~1 nm of defocus. Because the thermo-optic coefficient of water[11] at 193 nm, $dn/dT=-10^{-4}/°C$, is about 20 times higher than that of the traditional N_2 ambient, liquid temperature control is critical. Each 0.01 °C uncertainty in the bulk water temperature reduces the focus budget by ~1 nm.

During exposure, the wafer absorbs photons and heats up, and some of this heat is transferred to the immersion liquid. Numerical modeling of this heating process must take into account the scanning of the wafer which results in a liquid flow, which replaces heated liquid with fresh liquid under the lens. Some results of such a detailed numerical model[9] are reproduced in Fig. 2(a), which shows temperature profiles of the liquid at the trailing edge of the exposure slit for various flow conditions. While the temperature rises as much as 0.15 °C near the wafer surface in water immersion, the heat does not have time to diffuse throughout the bulk of the liquid. Its impact is thus much smaller than a similar shift in the bulk temperature. The temperature induced change in the optical path difference (OPD) between the axial and marginal rays is

$$\Delta\mathrm{OPD}=\Delta\mathrm{OPL}_{\mathrm{axial}}-\Delta\mathrm{OPL}_{\mathrm{marginal}}=\frac{dn}{dt}\left(\frac{1}{\cos\theta}-1\right)\int_{\mathrm{wafer}}^{\mathrm{lens}}\Delta T\,dz, \quad (2)$$

where ΔOPL is the change in optical path length (OPL) of each ray. The same ΔOPD can also be induced by moving the wafer plane out of focus:

$$\Delta\mathrm{OPD}=n(\cos\theta-1)\Delta\mathrm{focus}. \quad (3)$$

Combining Eqs. (2) and (3), we see that the equivalent focus shift for a coherent imaging system is

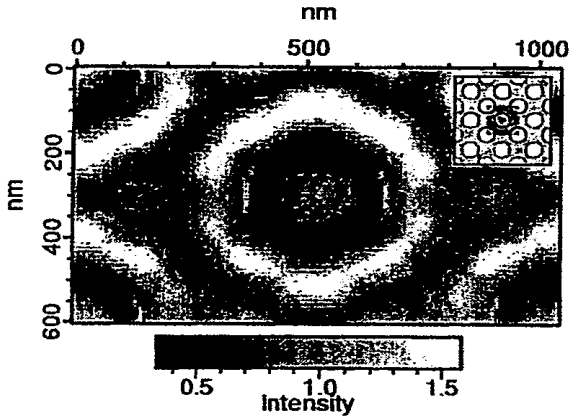


FIG. 3. Simulated aerial image of an array of gas bubbles 300 nm in diameter and 100 nm high on the resist surface. The spatial modulation of the intensity is 80%. Inset: Schematic of the gas bubble array. The shaded area in the center represents the area shown in the main part.

incident dose, with no thresholding behavior. Within the dose accuracy, the thickness removed was equal for wet and dry exposures. Atomic force microscope (AFM) inspection of the developed surfaces [Figs. 4(a) and 4(b)] showed little difference between wet and dry and certainly no evidence of bubbles at any dose. The Fourier spectral signature of the surface roughness [Fig. 4(c)] also revealed no significant difference between the dry and immersion exposures across the dose range measured.

V. CONTACT IMAGING

Another area of concern in immersion lithography is the possibility of interaction of the immersion liquid with the resist. Preliminary tests with blanket exposures suggest that, at least for some types of 193 nm resist, exposure to water

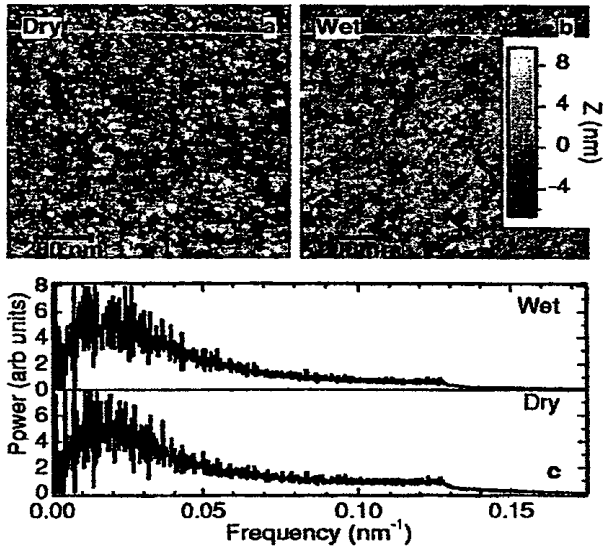


FIG. 4. AFM images of a gray tone resist exposed at 193 nm under (a) N_2 and (b) water ambient. No evidence of bubbles is seen. (c) The power spectral density of the surface roughness is virtually identical after wet and dry exposure.

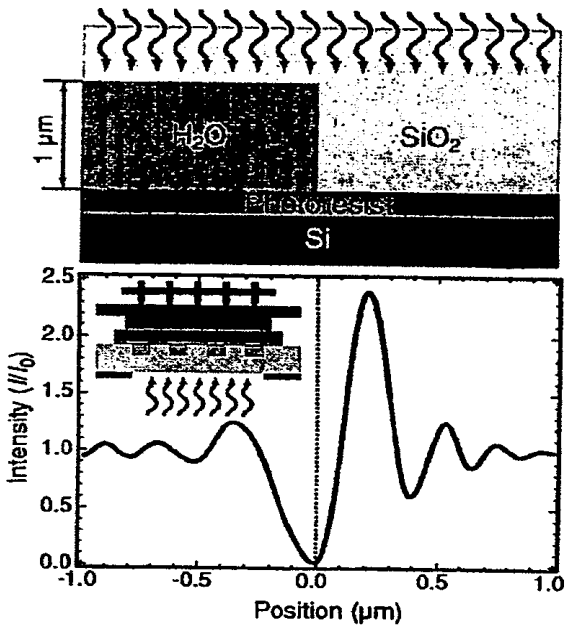


FIG. 5. Top: Schematic of the immersion phase-edge contact printing process. The relief in the phase mask is filled with water. Bottom: Simulated aerial image at the phase edge. Inset: Schematic of the simple jig used to achieve optical contact between the wafer and the mask. An array of fine pitched screws apply pressure, while the fringes are observed through the mask from below.

causes little to no change in resist thickness or surface energy.[14] Recently, we have performed a series of experiments which determined the elemental composition of 193 nm photoresists exposed to water with and without irradiation. These x-ray photoelectron spectroscopy (XPS) studies showed, among other effects, that water soluble base stabilizers are leached out of the resist almost immediately upon contact with water. However, the impact of such changes in resist composition on lithographic performance is still unclear. There is no substitute for high resolution imaging. In the absence of an immersion projection tool, we have adapted a phase-edge contact printing technique[19] which enables the patterning of sub-100 nm features with a simple apparatus. A jig consisting of an array of fine pitched screws (Fig. 5 inset) is used to bring a water covered, resist-coated wafer into optical contact with a fused silica phase mask. Using interference fringes as a guide, good contact can be established over almost all of the 50×50 mm^2 exposure area. Because this procedure is not carried out in a clean environment, a few dust particles typically create localized (1–3 mm diam) areas of poor contact. The resist is then exposed through the mask. Because water fills the relief of the mask, phase edges must be etched to a depth d which yields an optical path difference, $\mathrm{OPD}=d(n_{\mathrm{mask}}-n_{\mathrm{liquid}})=\lambda/2$ between the light transmitted through the glass and that transmitted through the water; with a fused silica mask at 193 nm, $d\approx 1\ \mu$m. A diagram of the contact at a single phase edge as well as a numerical simulation of the resulting aerial image are shown in Fig. 5. This technique easily yields features with ~100 nm linewidths. Figure 6 shows scanning electron microscope (SEM) micrographs of exposures of a 300 nm

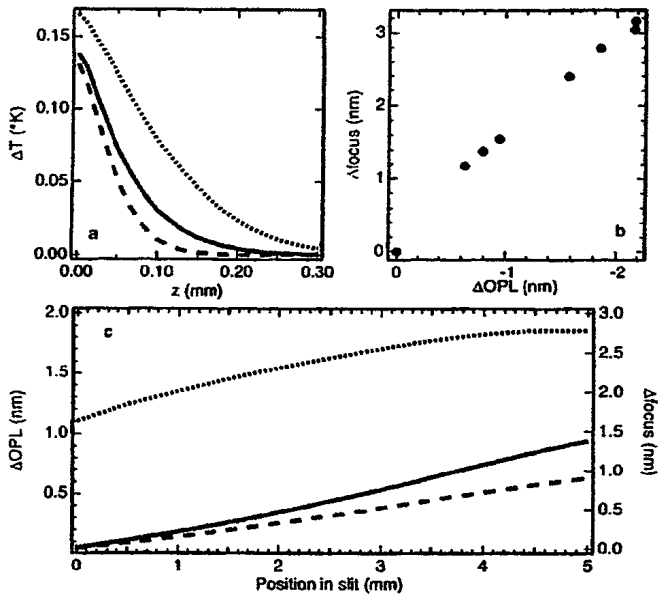


FIG. 2. Numerical modeling of the effect of temperature gradients in the fluid. (a) Temperature gradients at the trailing edge of a water immersion exposure slit (after Ref. 9). The dashed line represents fluid injection at 1 kPa parallel to the scan direction, the dotted line at 1 kPa antiparallel to the scan, and the solid line at 0 Pa. The wafer is at $z=0$ and the lens surface at $z=1$ mm. (b) Numerically modeled focus shift due to temperature gradients as a function of the integrated change in optical path length. (c) Optical path length and focus differences across the 5 mm exposure slit. The leading edge is at 0 and the trailing edge, corresponding to the gradients shown in (a), is at 5 mm.

$$\Delta\text{focus} = -\frac{\Delta\text{OPL}_{\text{axial}}}{n\cos\theta} = -\frac{\Delta\text{OPL}_{\text{axial}}}{\sqrt{n^2-\text{NA}^2}}. \tag{4}$$

For water immersion at NA=1.3, $\Delta\text{focus} = -1.6\,\Delta\text{OPL}_{\text{axial}}$. These analytical results were confirmed by numerical simulations in which the liquid was broken into layers and the index of each layer adjusted to match these one-dimensional (1D) temperature profiles. The resulting shift in best focus, shown in Fig. 2(b), is $-1.5\,\Delta\text{OPL}_{\text{axial}}$ with the difference from the analytical results due to the partial coherence modeled in the simulations. In reality, a temperature profile also induces spherical aberrations of various orders but they are quite small. Even the most extreme temperature gradients simulated showed no change in contrast at best focus. For realistic scanning parameters, total focus shifts of 1–3 nm can be expected, depending on the flow conditions. This shift constitutes a small but nonnegligible portion of the focus budget.

The temperature profile in the liquid is, of course, not one dimensional, even in the case of uniform illumination. The primary two-dimensional (2D) effect is the difference in temperature between the leading and trailing edges of the exposure slit. The fluid at the trailing edge has absorbed more energy and has had more time for the heat to propagate. It is thus hotter through more of its thickness than the liquid at the leading edge which remains near the ambient temperature. This results in a difference in focus (tilt) across the 5 mm slit of approximately the same magnitude as the overall focus offset [Fig. 2(c)]. We have recently extended our optical simulation capability to take this 2D temperature profile into account, and our initial results are in agreement with the estimates based on 1D results shown here.

A final possible source of heating which has not yet been considered is the viscous heating caused by flow. This should be a small effect for water, but may be significant for other liquids such as those under study for use at 157 nm, and may indeed prove to be the most important factor limiting acceptable liquid viscosity.

IV. BUBBLES

The exposure ambient of a conventional lithographic exposure system is a gas where spatial inhomogeneities due to changes in pressure or composition are small. In immersion lithography, however, there is the possibility of large index inhomogeneity due to bubbles in the immersion liquid. Microscopic bubbles (~10 μm and larger) can be formed in the liquid handling system by entraining gas from the outside during scanning[15] or by devolution of dissolved gas due to temperature or pressure changes in the liquid. The former can be avoided by careful fluidic design and the latter by removing the dissolved gas from the water (degassing). Bubbles could also arise from the outgassing of resists under exposure. Using conservative estimates: free diffusion of gas from the resist into the water, a high peak outgassing rate (10^{15} molecules $\text{cm}^{-2}\,\text{s}^{-1}$; equivalent to the IBM V2 experimental resist[16]), and a high gas diffusion rate in the resist ($10^{-8}\,\text{cm}^{-2}\,\text{s}^{-1}$), the peak concentration of a common outgassing product, isobutene, in water is ~250 $\mu\text{g}\,\text{cm}^{-3}$ below but not far below the 340 $\mu\text{g}\,\text{cm}^{-3}$ solubility limit.[17] Direct experimental verification of the effect of outgassing is clearly required and experiments are ongoing at Lincoln Laboratory to measure the formation of bubbles from a variety of resists.

There is also some evidence that large numbers of nanobubbles with 10–100 nm thickness may form spontaneously at hydrophobic surfaces[18] due to the energetic advantage of having a gas layer isolating the water from the surface. The formation of such bubbles on a resist surface would be disastrous for immersion lithography. Figure 3 shows a numerical simulation of the aerial image created by blanket exposure through an array of bubbles 300 nm in diameter and 100 nm high at the surface of the resist. Instead of a uniform image, the intensity is modulated by 80%; any such bubble would almost certainly cause a printable defect. Simulations with bubbles as little as 10 nm high show 30% modulation in image intensity. It is thus critical for immersion lithography to establish whether such bubbles form at resist–liquid interfaces.

Because bubbles at the resist surface are predicted to have such a large impact on the aerial image, blanket exposures of water coated resist should reveal their presence. Wafers coated with 1 μm thick hydrophobic (unexposed water contact angle 80°) gray tone resist were exposed at doses from 1 to 1000 $\text{mJ}\,\text{cm}^{-2}$ under both N_2 and water ambient in an open frame exposure system. The thickness of resist removed upon development was proportional to the log of the

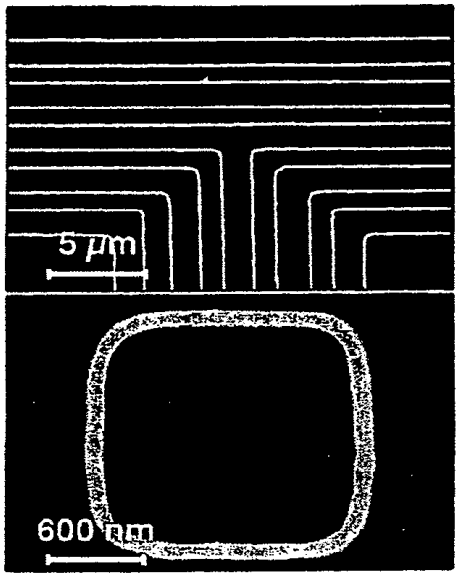


FIG. 6. SEM micrographs of 300 nm bilayer resist exposed at 193 nm with immersion phase-edge contact printing. The linewidth in both images is 100 nm.

thick bilayer resist[19] which show no evidence of defects due to bubble formation or water–resist interaction. More extensive tests of model 193 nm resists are planned along with a study of the impact of immersion liquid impurities on resist performance.

VI. FLUIDS FOR 157 nm IMMERSION

While water appears to be the preferred immersion liquid at 193 nm, fundamental work remains in the identification of a suitable fluid for 157 nm use. The primary issue and the focus of our research to date is the lack of sufficiently transparent liquids at this wavelength. Liquid absorbance is determined by measuring the transmission of cells consisting of the liquid sandwiched between two CaF_2 windows held apart by a spacer whose thickness determines the path length x in the liquid. Measurements of three cells with $x = 5\ \mu m - 1$ mm fit to Beer's law, $T = T_0 10^{-\alpha x}$, yield liquid absorbance α. The error (1σ) is on the order of 0.3 cm^{-1}, principally due to cell-to-cell differences in the transmission of the CaF_2 windows, T_0, which can vary by a few percent at 157 nm. The accuracy can be improved by an order of magnitude by measuring the same cell (i.e., the same windows) three to five times with different spacers.

Initial studies[10] focused on perfluorinated polyethers (PFPEs) which are available commercially as high performance pump oils and heat transfer fluids. The absorbance of these materials as received from their manufacturers was found to be, at best, 6 cm^{-1}, which would permit a working distance of less than 40 μm at 95% transmission. This "as received" absorbance can be reduced in several ways, for example, by the elimination of dissolved oxygen. In air, perfluorocarbon liquids dissolve large amounts of O_2 which contribute a significant portion of the overall absorbance at 157 nm. This O_2 can be removed, either by sparging with N_2 gas or by repeated cycles of freezing, pumping, and thawing under vacuum. De-oxygenated PFPEs with absorbances as low as 3 cm^{-1} were found. Even with the removal of O_2, however, nuclear magnetic resonance (NMR) and gas chromatography/mass spectrometry (GCMS) reveal these PFPEs to be complicated systems with polydisperse molecular weights and defects in the polymer backbone, making systematic study of the absorbance difficult.[14]

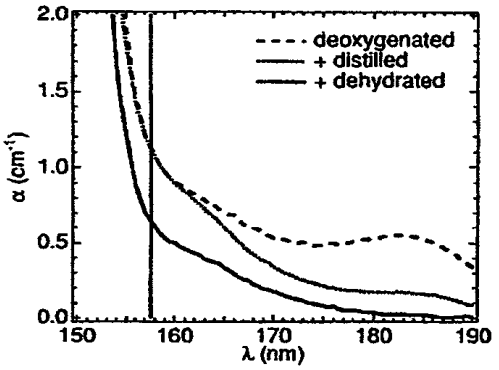


FIG. 7. Absorbance of perfluorotriglyme after de-oxygenation (dashed line), distillation followed by de-oxygenation (dotted line), and distillation followed by de-oxygenation and dehydration.

Studies of simpler perfluorocarbon and hydrofluorocarbon systems have emphasized that liquid purity is the key to low absorbance at these short wavelengths. With low molecular weight materials, routine use of GCMS can ensure that low levels of contaminants do not dominate the measured absorbances. Under these conditions, very low values of absorbance can be found. The lowest absorbance material measured to date is perfluorotriglyme (PFTG, $CF_3[OCF_2CF_2]_3OCF_3$). With the oxygen removed, PFTG has a 157 nm absorbance of 1.12 ± 0.08 cm^{-1} (Fig. 7), yielding a 200 μm working distance at 95% transmission. GCMS analysis reveals the presence of trace levels of contaminants, principally chlorofluorocarbon and unsaturated fluorocarbon species which can be partially removed by distillation. We estimate that even 1 ppm of chlorofluorocarbon can contribute ~0.5 cm^{-1} to the 157 nm absorbance. As seen in Fig. 7, while distillation improves the absorbance at longer wavelengths, the effect at 157 nm is not significant. Finally, at these low absorbances, the ppm levels of water dissolved in the perfluorocarbons are significant. When this moisture is reduced by treatment with a silica based drying agent, the 157 nm absorbance of PFTG is 0.64 ± 0.07 cm^{-1}, the current record for low absorbance of an organic liquid and low enough for a 350 μm working distance.

VII. CONCLUSIONS AND FURTHER WORK

Immersion lithography can improve the resolution of projection optics and should allow the extension of optical lithography beyond 50 nm. At 193 nm, water appears to be the immersion liquid of choice, and work is ongoing to discover potential issues with its use. To date, no show-stopping problems have been identified. Areas of concern remain, however, including bubble formation from resist outgassing, po-